

SELECTIVE CATALYTIC OXIDATION OF CO IN H₂ FOR FUEL CELL APPLICATIONS

Olga Korotkikh and Robert Farrauto
Engelhard Corporation
101 Wood Avenue
Iselin, New Jersey 08830-0770

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ABSTRACT

A critical issue for the PEM fuel cell is the ability to delivery clean H₂ to the anode electrode the kinetics of which are greatly hindered by traces of CO present from the hydrocarbon steam reforming and water gas shift processes. A technology receiving much attention is the selective oxidation of CO to CO₂. Ideally the catalyst must selectively oxidize about 1% (10,000 ppm) CO to less than 5 ppm without oxidizing any of the 30-70% H₂ present.

This paper will describe performance results of a newly developed catalyst for selective oxidation of CO for PEM fuel cell applications. The effect of space velocity, concentrations of CO, O₂/CO ratios and temperature on activity and selectivity will be presented.

INTRODUCTION

Development of the proton exchange membrane (PEM) fuel cell has been considerable during the last 10 years advancing the commercial possibilities for generating clean and efficient power for stationary and mobile source applications (1, 2). The system operates at about 70-80°C using H₂ as the anode fuel. Given the extensive infrastructure existing for natural gas (stationary source applications) and gasoline (mobile source) these are the preferred sources of H₂. The production of clean H₂ for the chemical industry from hydrocarbon feeds (3) is accomplished by a series of catalytic steps including desulfurization, steam reforming, water gas shift and CO removal by either selective oxidation, methanation or pressure swing absorption. All of these technologies are now being reviewed for possible use in the fuel cell.

In the early 1960's Engelhard developed and commercialized the Selectoxo™ catalyst and process for H₂ plants (4-6). The heart of this technology is a highly selective catalyst, which oxidizes up to 10,000 ppm CO without significantly oxidizing the 70% H₂ (dry) present. CO levels were reduced to less than 5 ppm under steady state conditions (50°C, 10,000 h⁻¹ and 200-400 psig). The Selectoxo™ system was located downstream from the CO₂ and H₂O scrubber. For fuel cell applications the catalyst must operate at much higher space velocities at temperatures above about 90°C at ambient pressure in the presence of large amounts of CO₂ and H₂O. Furthermore, it must be designed for transient operation since power demands will vary considerably depending on the application. A large consumption of H₂ is undesirable since it decreases power generation and complicates heat management. Therefore, having a catalyst with high selectivity is critical.

EXPERIMENTAL

The Selectoxo™ catalyst contains 0.5% Pt supported on γ -alumina 1/8 inch tablets promoted with a base metal oxide. The alumina is impregnated with salts of Pt and base metal oxide, dried and calcined. The composition of the new catalyst has been modified and prepared as a powder suitable for deposition onto a monolith structure. We call this material monosel. The cordierite monolith is 400 cells per square inch and is dipped into a water slurry of the catalyst, dried and calcined. Typically washcoat loading of about 1.5 g/in³ were obtained. For direct testing of powdered catalysts they were pressed and crushed into particles 40-60 microns in size.

The test gas contained between 1000 and 5000 ppm CO, 20 % H₂, 10% H₂O and varying O₂ to CO ratios with the balance N₂. When powders were tested they were diluted in a 1:2 ratio of catalyst to quartz. Monoliths were wrapped with insulation and fitted into the 1 inch ID quartz reactor. A control thermocouple was positioned in the inlet section of the catalyst bed.

The consumption of CO and generation of CO₂ was measured with a California Analytical Instruments infrared gas analyzer. O₂ consumed was measured with a Rosemount electrochemical analyzer. The generation of hydrocarbons was monitored with a Rosemount Analytical flame ionization analyzer, but under the conditions of these experiments here none was ever detected.

RESULTS

The comparison of powdered $\text{Pt}/\text{Al}_2\text{O}_3$ with monosel, at equal concentrations of Pt, at 90 and 150°C and O_2/CO ratios of 0.5 and 0.75 are shown in Table 1. The powder volumetric space velocity (VHSV) is 120,000 h^{-1} . The presence of the promoter metal oxide in monosel significantly increases the CO activity and conversion (X_{CO}) while maintaining excellent selectivity of O_2 for CO ($X_{\text{O}_2 \text{ for CO}}$). Under all conditions the $\text{Pt}/\text{Al}_2\text{O}_3$ never obtains high CO conversions relative to monosel under realistic operating temperatures up to 150°C.

Figures 1 and 2 demonstrate the influence of oxygen excess above stoichiometric at different temperatures and space velocities for monosel deposited on a monolith. At 90°C and a VHSV of 20,000 hr^{-1} increasing oxygen improves the activity of the catalyst, but the selectivity decreases. At $\text{O}_2/\text{CO} = 1$ conversion of CO reaches 100% with the O_2 selectivity for CO about 50% (Figure 1).

Raising the temperature to 150°C (Figure 2) at a monolith VHSV of 80,000 hr^{-1} gives almost 100% CO and O_2 conversions at $\text{O}_2/\text{CO} = 1.5$. The O_2 selectivity for CO is 33%.

The results for 2000 and 5000 ppm CO are presented in the Table 2. At 90°C increasing the CO concentration from 2000 to 5000 ppm, under stoichiometric conditions ($\text{O}_2/\text{CO} = 0.5$), shows a constant CO conversion of 69%. The selectivity of O_2 for CO improves from 66 to 77.6%. Increasing the O_2/CO ratio to 0.75 increases CO conversion to almost 97% with similar selectivities of 64 vs. 68%. At $\text{O}_2/\text{CO} = 1.0$ the CO conversion reaches 100% while the selectivity decreases to about 50%. At 150°C 100 % conversion of CO is achieved at both 2000 and 5000 ppm at an $\text{O}_2/\text{CO} = 1$ with selectivities of about 50%. As the O_2/CO conversion is decreased from 0.75 to 0.5 the CO conversion decreases, but the total O_2 conversion remains almost 100% with an O_2 selectivity for CO of about 58% for 2000 ppm and 65% at 5000 ppm.

CONCLUSIONS

1. At 90°C, VHSV = 20,000 hr^{-1} and $\text{O}_2/\text{CO} = 1$ conversion of CO is about 100% with the O_2 selectivity for CO about 50%.
2. At 150°C, VHSV = 80,000 hr^{-1} and $\text{O}_2/\text{CO} = 1.5$ conversion of CO is about 100% with the O_2 selectivity for CO about 33%.
3. CO conversions of 100 % are achievable at $\text{O}_2/\text{CO} = 0.75$ (at 5000 ppm) and 1 (at 2000 ppm).
4. At 150°C, 100% CO conversion is obtained at an $\text{O}_2/\text{CO} = 1$. Selectivity of O_2 for CO is about 50%.

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Table 1
Comparison of Powdered Pt/Al₂O₃ and Monosel Catalysts
(fraction 40-60 μ , VHSV~120,000 hr⁻¹)

#	TEST CONDITIONS	Monosel		Pt/Al ₂ O ₃	
		Xco, %	Xo ₂ for CO, %	Xco, %	Xo ₂ for CO, %
1.	At 90°C, O ₂ /CO=0.5	51	78	13.2	82
2.	At 90°C, O ₂ /CO=0.75	90	65	12.7	66.2
3.	At 150°C, O ₂ /CO=0.5	52.7*	61.6*	26.8	56.7

*) data were obtained with monosel on a monolith at a VHSV = 80,000 h⁻¹

Table 2
Effect of CO Concentration on Monosel Performance

#	TEST CONDITIONS	2000 ppm CO			5000 ppm CO		
		Xco, %	Xo ₂ , %	Xo ₂ for CO %	Xco, %	Xo ₂ , %	Xo ₂ for CO %
1	At 90°C, O ₂ /CO = 0.5	68.9	98.1	66.1	69.0	87.0	77.6
2	At 90°C, O ₂ /CO = 0.75	96.8	97.5	64.4	100	99.7	68.1
3	At 90°C, O ₂ /CO = 1.0	100	99.6	50.7	-	-	-
4	At 150°C, O ₂ /CO = 1.0	100	99.7	50.6	100	100	50.9
5	At 150°C, O ₂ /CO = 0.75	90.6	99.5	57.8	97.5	100	64.6
6	At 150°C, O ₂ /CO = 0.5	61.2	99.2	57.7	65.6	99.4	64.6

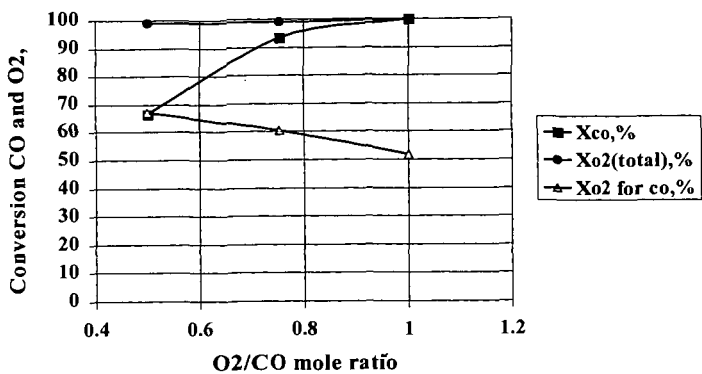


Fig. 1. Monosel on monolith activity and selectivity depends on O₂/CO (90°C, 1,000 ppm CO, 20% H₂, 10% H₂O, VHSV=20,000 hr⁻¹)

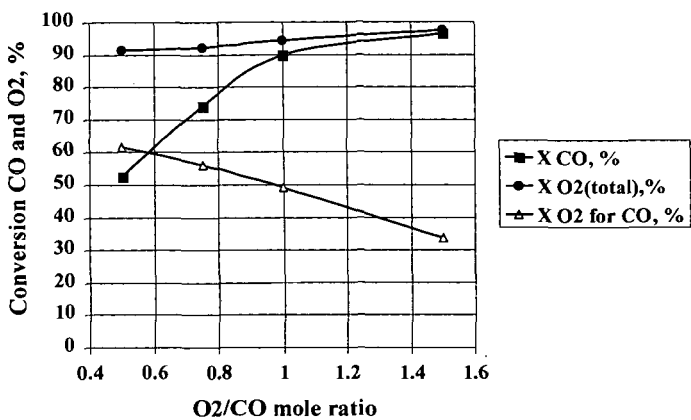


Fig. 2. Monosel on monolith activity and selectivity depends on O₂/CO mole ratio (150°C, 1,000 ppm CO, 20% H₂, 10% H₂O, VHSV=80,000 hr⁻¹)